ON THE DISSOLUTION VELOCITY OF OXYGEN INTO WATER. PART V. THE OXIDATION VELOCITY OF SODIUM SULPHITE SOLUTION BY OXYGEN IN THE PRESENCE OF THE MOLECULAR FILM OF FATTY ACID.

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Introduction.

H. Davis and R. Schuler[1] carried out a research on the rate of absorption of the gaseous olefins into sulphuric acid solution and found that the specific absorption coefficient (volume of gas absorbed per second per square centimeter of surface) was not appreciably affected by the agitation of the main body of the liquid. Ethylene was absorbed by concentrated sulphuric acid as rapidly when the acid was quiescent as when it was stirred (without breaking the surface or changing its area) at 400 revolution per minute.

H. Davis and G. Crandall[2] studied the rate of the solution gaseous olefines into sulphuric acid solution with an apparatus newly devised, and obtained exactly the same result as that of the above mentioned experiment.

According to Nernst,[3] an unstirred stationary liquid layer exists at the upper surface of liquid which is in contact with gas.

Whitman and Keats[4] extended the theory of Nernst, and proposed an assumption that whenever a liquid and a gas come into contact there exists on the gas side of the interface a layer of gas in which motion by convection is slight compared with that in the main body of the gas, and similarly on the liquid side of the interface there is a surface layer of the liquid which is practically free from mixing by convection.

The theoretical interpretations of the rate of absorption of gaseous olefins by sulphuric acid solution and of the rate of absorption of carbon dioxide by sodium hydroxide solution, given by Davis and Crandall,[5] are based on the theory of whitman and Keats, the two-film theory.

Davis and Crandall[5] have made two suppositions; firstly that the reactions take place instantaneously in the liquid film, and secondly that the

(1) *J. Am. Chem. Soc.*, **52** (1930), 721.
(2) Ibid., **52** (1930), 3757.
(3) *Z. physik. Chem.*, **47** (1904), 52.
(4) *J. Ind. Eng. Chem.*, **14** (1922), 185.
(5) Loc. cit.

upper surface of the liquid film, which is not disturbed by the agitation of the main body of the liquid, is kept at the saturated state with the gas. From these assumptions it is quite easy to see that the velocity of the absorption depends only upon the velocity of diffusion of the gas molecules and that of the molecules of the reacting substances through the stationary liquid film. Davis and Crandall[1] proposed the following equation for the initial rate of absorption of gas into a well-stirred liquid when any irreversible chemical reactions taking place are instantaneous, compared with the rate of solution of the gas.

$$\frac{1}{S}\left(\frac{dn}{dt}\right)_{Initial} = k(c_\infty + c_m),$$

where $\frac{1}{S}\left(\frac{dn}{dt}\right)_{Initial}$ is the initial rate of absorption of the gas per unit area of the surface, S the area of the boundary surface, k a constant, c_∞ the saturation concentration of the dissolved gas and c_m the concentration of the reacting solute.

The oxidation of sodium sulphite solution[2] by means of oxygen is quite an analogous phenomenon. But from the results of the experiments of the present writers[2] it was found that the velocity of the oxidation of sodium sulphite solution does not increase above a certain maximum value, however much the concentration of sodium sulphite be increased.

The above mentioned equation, proposed by Davis and Crandall, will be unsuitable for the interpretation of this phenomenon, and it might be immediately supposed that it would be necessary to make suppositions different from those proposed by Davis and Crandall in order to interprete the velocity of oxidation of sodium sulphite solution.

The following facts were already ascertained by one of the present writers (Miyamoto) experimentally.

(1) The maximum velocities of the oxidation of sodium sulphite, stannous hydroxide and ferrous hydroxide in sodium hydroxide solutions are identical under the comparable conditions.[3]

(2) The velocities of oxidation of these oxidizable substances do not increase above this maximum value with the increase of the concentration of these substances, as was above mentioned.

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(1) Loc. cit.

(2) S, L. Bigelow, *Z. physik. Chem.*, **26** (1898), 493; S. Miyamoto, this Bulletin, **2** (1927), 74; S. Miyamoto and T. Kaya, ibid., **5** (1930), 123; S. Miyamoto, T. Kaya and A. Nakata, ibid., **5** (1930), 229; S. Miyamoto and T. Kaya, ibid., **5** (1930), 321; S. Miyamoto and A. Nakata, ibid., **6** (1931), 9.

(3) S. Miyamoto, this Bulletin, **2** (1927), 74; ibid., **2** (1927), 155; ibid., **3** (1928), 98; ibid., **3** (1928), 137.

(3) The total oxidized quantity of these substances during a definite time interval does not increase by mixing them.[1]

(4) The maximum oxidation velocity of sodium sulphite solution is proportional to the area of the interface of oxygen and the solution.[2]

From these facts one of the present writers (Miyamoto) made the assumption that the maximum velocity of oxidation of sodium sulphite solution will be equivalent to the initial rate of solution of oxygen into water, in the surface of which no free oxygen is present.

This supposition was endorsed by the comparison[2] of the initial rate of solution of oxygen into water obtained from the result of the direct measurement by several writers[3] with that calculated from the velocity of oxidation of sodium sulphite solution.

For the theory of the rate of solution of gases into liquids, proposed by one of the present writers[4] (Miyamoto), a part of which was stated in the previous paper, it is a matter of indifference whether the thin liquid film (the diffusion layer), at the upper surface of the liquid phase, is agitated by the stirring of the main body of the liquid or not. Only the second supposition, proposed by Davis and Crandall, that the upper surface of the liquid film is instantaneously saturated with the gas, seems to be unprobable for the interpretation of the velocity of oxidation of sodium sulphite solution.

If the thin stationary liquid film be really not disturbed by the agitation of the main body of the liquid, as was supposed by several writers, the occurrence of the following phenomenon will be expected.

When the molecules of fatty acid were placed at the upper surface of sodium sulphite solution by a proper method, they occupy a certain area of the surface, undisturbed by the agitation of the main body of the solution, and the velocity of oxidation of sodium sulphite solution, which is equivalent to the initial rate of solution of oxygen under certain conditions, will change as a result of the alteration of the area of the free boundary surface between gas and liquid. Then it will be possible to calculate the effective area of a molecule of fatty acid from the measurement of the velocity of oxidation of sodium sulphite solution in the presence of a measured quantity of fatty acid, as the maximum velocity of the oxidation of sodium sulphite solution was confirmed to be proportional to the area of the boundary surface.

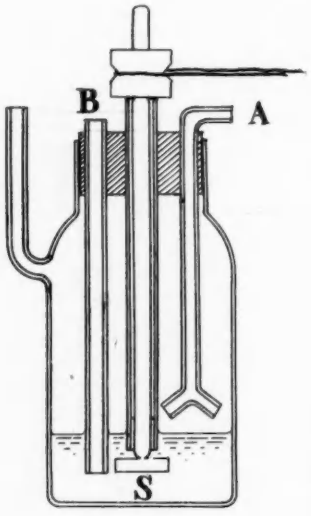
(1) S. Miyamoto, this Bulletin, **2** (1927), 191; ibid., **4** (1929), 132.
(2) S. Miyamoto and A. Nakata, ibid., **6** (1931) 9.
(3) Adeney and Becker, *Phil. Mag.*, **38** (1919), 317; **39** (1920), 385; **42** (1921), 87; Davis and Crandall, *J. Am. Chem. Soc.*, **52** (1930), 3757, 3769.
(4) Loc. cit.,

The cross-sections and the length of many organic compounds were obtained from the result of excellent physical experiments by Langmuir[1] and by Adam.[2]

The present research was carried out with the expectation that the relation between the effective cross-section of the molecule of fatty acid, which will be calculated from the measurement of the velocity of the oxidation of sodium sulphite solution in the presence of the molecules of fatty acid, and the real cross-section obtained from the result of physical experiment will be obtained.

Experimental.

The apparatus, graphically shown in the accompanying figure, was employed as the reacting vessel. The apparatus has nearly the same construction as that employed in the previous research.[3] The important difference, which will be seen by the comparison of the present apparatus with that stated in the previous paper, is that the lower end of the tube B is dipped in the solution in the present case.



The experimental method is as follows.

A definite quantity of fatty acid was dissolved in a definite volume of purified, newly distilled benzene, and by means of a calibrated pipette a few drops of the bezene solution of fatty acid was added on the measured quantity of water contained in the vessel, which was placed in a water thermostat. Air, washed by acidified potassium bichromate and sodium hydroxide solutions, was passed at a high velocity through A for about an hour to remove benzene completely from the apparatus. After the benzene has been perfectly evaporated off, oxygen, washed by the above mentioned reagents, was passed into the apparatus at a high velocity through A for about thirty minutes. When the air in the apparatus has been entirely replaced by oxygen, the

(1) *J. Am. Chem. Soc.*, **39** (1917), 1848.
(2) *Proc. Roy. Soc.*, **99** A (1921), 336; **101** A (1922), 452, 516; **103** A (1923), 676, 687.
(3) S. Miyamoto and A. Nakata, This Bulletin, **6** (1931), 11.

stirrer is put in motion at the rate of about 400 revolutions per minute and the rate of the passage of oxygen was regulated at about 15 liters per hour.

The stop-watch was started when about half the volume of sodium sulphite solution had been added in the vessel through B, the total volume of the solution being made up to 40 c.c. . The quantity of sodium sulphite solution added was determined separately by the usual method of iodometry.

When t-minutes have elapsed, the revolution of the stirrer and the current of oxygen were stopped and nitrogen gas was passed from A in the apparatus at a high velocity to drive the oxygen out as quickly as possible.

The vessel was then taken out and the total quantity of the solution was poured into a known quantity of iodine solution, acidified with hydrochloric acid. After the reacting vessel had been repeatedly washed with distilled water, the excess of iodine was titrated back by means of sodium thiosulphate solution of 0.1000 normal.

Representative results of the experiments are given in Tables 1 and 2.

In the tables, v is the volume of sodium thiosulphate solution of 0.1000 normal, equivalent to the quantity of sodium sulphite remained in

Table 1. (Temp. = 25°C)

No.	Conc. of stearic acid solution moles / liter	Stearic acid solution taken c.c.	S_{acid} cm.^{2}	S_0 cm.^{2}	t min.	v c.c.	k	$\frac{k}{S_0}$
1	0	0	0	26.31	—	—	0.682	0.0259
2	0.879×10^{-4}	0.050	5.60	25.60	0 30	207.69 188.80	0.630	0.0246
3	,,	0.050	5.60	,,	0 30	211.29 190.51	0.693	0.0271
4	,,	0.100	11.20	,,	0 30	203.64 184.01	0.654	0.0255
5	,,	0.200	22.30	,,	0 30	205.25 184.37	0.696	0.0272
6	8.06×10^{-4}	0.050	51.30	,,	0 30	231.18 211.80	0.646	0.0252
7	,,	0.200	205.10	,,	0 30	207.68 188.01	0.656	0.0256
8	43.72×10^{-4}	0.034	189.10	,,	0 30	227.48 208.02	0.649	0.0254
9	,,	0.200	1113.00	,,	0 30	206.50 187.00	0.650	0.0254

Table 2. (Temp. = 25°C)

No.	Conc. of palmitic acid solution moles / liter	Palmitic acid solution taken c.c.	S_{acid} cm.^{2}	S_0 cm.^{2}.	t min.	v c.c.	k	$\frac{k}{S}$
1	0	0	0	26.31	—	—	0.682	0.0259
2	1.125×10^{-4}	0.033	4.72	25.5	0 30	232.47 212.22	0.675	0.0265
3	3.707×10^{-4}	,,	15.57	,,	0 30	237.25 217.54	0.657	0.0258
4	8.125×10^{-4}	,,	34.12	,,	0 30	236.28 217.05	0.641	0.0251
5	18.37×10^{-4}	,,	77.14	,,	0 30	236.58 217.51	0.636	0.249
6	41.60×10^{-4}	,,	174.70	,,	0 30	232.09 213.77	0.611	0.0240

the solution, when t-minutes has passed from the moment at which the oxidation had taken place.

The values k, given in the third column of the tables, were calculated according to the equation.

$$k = \frac{v_0 - v}{t},$$

where v_0 is the value of v at $t = 0$.

The values of S_{acid}, given in the 4th column of the tables, stand for the area, which would be occupied by the molecules of fatty acid added, if they formed a monomolecular film, and the values were calculated in the following manner.

According to the investigations of Langmuir[1] and Adam,[2] when a few drops of benzene solution of fatty acid was placed on the surface of water, the molecules of fatty acid are arranged not indiscriminately but perpendicular to the surface and parallel to each other after the benzene has been evaporated off.

If the thin stationary layer at the surface of the solution be not disturbed by the agitation of the main body of the solution with a stirrer, the orientation of the molecules of fatty acid will take place during the present observation in exactly the same way as in the case of quiescent water. From

(1) Loc. cit.
(2) Loc. cit.

this assumption the values S_{acid} were calculated from the quantity of fatty acid solution taken and the area of the cross-section of each molecule, for which 21×10^{-16} cm^2., obtained by Adam,[1] was adopted for stearic acid and palmitic acid.

The area of the boundary surface between liquid and gas in the absence of the molecules of fatty acid was calculated by exactly the same process, as that stated in the previous paper,[2] and the value is given as S in the 5th column of the tables.

The value of k in the absence of the molecules of fatty acid, given in the tables, is the value already obtained in the previous experiment.[3]

As will be seen in the tables, the difference between the value of k observed in the absence of fatty acid and that observed in the presence of fatty acid lies in the range of experimental error, and it may be described that the presence of the molecules of fatty acid has virtually no effect on the oxidation velocity of sodium sulphite solution, which will be equivalent to the rate of solution of oxygen into water, which is free from oxygen, under the condition of the present experiments.

Discussion.

The molecules of these fatty acids employed will form a monomolecular or multimolecular film on the upper surface of the liquid after the complete evaporation of benzene. In the case of the experiments Nos. 2–5 in Table 1 and Nos. 2–3 in Table 2, a part of the boundary surface is covered with the monomolecular film, and in the case of the experiments Nos. 6–9 in Table 1 and Nos. 4–6 in Table 2, the total area of the boundary surface is occupied by the multimolecular film of the fatty acid.

According to the experiments of Adam,[4] the molecules of these fatty acids have the following magnitude.

	Cross section.		Length.
	Head. cm^2.	Chain. cm^2.	cm.
Palmitic acid.	25.1×10^{-16}	21.0×10^{-16}	23.7×10^{-8}
Stearic acid.	25.1×10^{-16}	21.0×10^{-16}	26.2×10^{-8}

(1) Loc. cit.
(2) Loc. cit.
(3) Loc. cit.
(4) Loc. cit.

The calculation of the thickness of the assumed stationary liquid film[1] was carried out by Brunner[2] and by Davis and Crandall,[3] and was based upon the assumption that the rate of solution of gases into liquids is no other than the velocity of diffusion of the gas molecules through the stationary liquid film at the interface. According to these writers, the thickness of the stationary liquid film is about 2×10^{-3}—2×10^{-2} cm., which naturally depends upon the rate of revolution of the stirrer in the main body of the liquid.

If the assumption, that a stationary film exists at the interface, be acceptable, the multimolecular film of fatty acid, whose thickness is a minute portion of that of the stationary film, will occupy the area of the upper surface of the interface during the measurements of the present experiments, undisturbed by the agitation of the main body of the liquid. From this consideration it will quite be probable to expect that the presence of the multimolecular film of fatty acids at the upper surface will have some effect on the rates of solution of gases into liquids.

The result of the present experiments was contrary to this expectation, and it will be difficult to interprete the present result by the ordinary theory, which is based upon the supposition of the presence of a stationary liquid film.

One of the present writers (Miyamoto) has an opinion that it will be very probable to interprete the process of solution of gases into liquids by the assumption that among the molecules which collide with the liquid surface only those molecules, whose components of velocity at right angles to the boundary surface are greater than a threshold value u_0, are able to enter into the the liquid phase. According to this supposition, the rate of solution will be expressed by

$$D_0 = N''S - N'''S,$$

where N'' is the number of the molecules which enter into the liquid phase through the unit area of the boundary surface per unit of time, N''' the number of the molecules which leave the liquid phase through the unit area of the boundary surface per unit of time and S the area of the boundary surface.

So long as the concentration of the gas in the liquid phase is maintained at zero, the rate of solution is given by

$$D_0 = N''S,$$

(1) Nernst, *Z. physik. Chem.*, **47** (1904), 52; Whitman and Keats, *J. Ind. Eng. Chem.*, **14** (1922), 185.
(2) *Z. physik. Chem.*, **47** (1904), 99.
(3) *J. Am. Chem. Soc.*, **52** (1930), 3760.

N''' being zero under this condition.

As was stated in the previous paper,[1] the oxidation velocity of sodium sulphite solution of proper concentration is equivalent to the value D_0, when the main body of the liquid is well agitated with a stirrer.

According to this theory of the rate of solution of gas into liquid, it is quite enough for the interpretation of the result of the present experiments if only one of the following assumptions be satisfied.

(1) The value u_0 does not differ whether the molecules of fatty acids are present or not.

(2) The liquid film at the interface is not stationary and the molecules of fatty acids are covered with the solution when the main body of the solution is agitated.

The present writers consider that the first assumption will be inadequate to be adopted.

If the second supposition be satisfied, the total area of the boundary surface is not altered by the addition of fatty acids, and the concentration of oxygen at the upper surface will be kept at zero by the presence of the sufficient quantity of sodium sulphite to react with all of the molecules of oxygen which enter into the liquid phase, so long as the main body of the liquid is well agitated with a stirrer.

It is then quite clear that the presence of the molecules of fatty acids will have no effect on the velocity of the oxidation of sodium sulphite solution, which is equivalent to the initial rate of solution of oxygen into water, D_0, under the present conditions.

For this interpretation it is of no use to investigate whether the molecules of fatty acids, covered with the solution, remain in the upper layer of the liquid or go down into the main body of the liquid during the experiments.

From the discussion, above stated, it seems that the supposition of the existence of the stationary liquid film of proper thickness, proposed by several writers, the diffusion theory, will be unfavourable to the interpretation of the result of the present experiments.

As the conclusion of the present research it will be possible only to describe that the thickness of the stationary liquid film, if it exist, should be smaller than the length of the molecule of palmitic acid, 23.7×10^{-8} cm., when the main body of the liquid is well agitated with a stirrer.

Although the present research failed to produce the expected result, the phenomenon observed will be one of the important experimental facts,

(1) Loc. cit.

which will be employed for the discussion of the process of solution of gasses into liquids.

As a result of the present research, it can be said that, under the conditions of the study on the rate of oxidation of sodium sulphite solution, carried out by Miyamoto and his collaborators, stationary liquid film does not exist at the boundary surface, and therefore the results of the experiments can not be interpreted by the classical theory, based upon the assumption that the phenomenon is the rate of diffusion through a stationary film at the interface.

Summary.

(1) The monomolecular or multimolecular films of stearic acid or of palmitic acid were formed at the upper surface of sodium sulphite solution, and the velocity of the oxidation of sodium sulphite solution was studied, the main body of the solution being well agitated with a stirrer of special construction. It was confirmed that the velocity of the oxidation of sodium sulphite solution by oxygen, observed in the presence of the molecules of these fatty acids, and that observed in the absence of the molecules of the fatty acids, are almost identical under the conditions above described.

(2) A short discussion on the result of the present experiments was made.

The assumption, that a stationary liquid layer is present at the interface between gas and liquid, seems to be unfavourable to the interpretation of the phenomenon observed by the present writers. It was stated that the assumption, that the molecules of fatty acid at the upper surface of the liquid will also be agitated by the stirring of the main body of the liquid and covered with the solution, has great probability for the interpretation of the result of the present experiments.

(3) The mechanism of solution of gas into liquid was shortly discussed.

A part of the opinion of one of the present writers (Miyomoto) on the rate of solution of gases into liquids was described.

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SOLUBILITIES OF METALLIC CYANIDES.

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In the author's previous paper[1] the solubilities of cyanide and thiocyanate of silver in water were published. Sherrill[2] determined the solubility of mercuric cyanide in water. But we have no information on the solubilities of cyanides of other metals. Author measured, hence, the solubilities of cyanides of cadmium, zinc, nickel, and cobalt.

In order to determine these solubilities the following cells are used.

$$\text{Cd (amalgam)},\ \text{Cd}^{++}\ (a_1)\ \|\ \text{Ca}^{++}\ (a_2),\ \text{Cd (amalgam)}$$
$$\text{Zn (amalgam)},\ \text{Zn}^{++}\ (a_1)\ \|\ \text{Zn}^{++}\ (a_2),\ \text{Zn (amalgam)}$$
$$\text{Ni (amalgam)},\ \text{Ni}^{++}\ (a_1)\ \|\ \text{Ni}^{++}\ (a_2),\ \text{Ni (amalgam)}$$
$$\text{Co (amalgam)},\ \text{Co}^{++}\ (a_1)\ \|\ \text{Co}^{++}\ (a_2),\ \text{Co (amalgam)}$$

The following two equations have been used to determine the electromotive force.

$$E_c = \frac{RT}{2F} \ln \frac{a_2}{a_1} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

$$E_l{}^{(3)} = \frac{\dfrac{\Lambda_C}{V_C} - \dfrac{\Lambda_A}{V_A}}{\Lambda_C + \Lambda_A} \frac{RT}{F} \ln \frac{a_2}{a_1} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

where E_c represents the electromotive force of electrodes, E_l, the liquid potential at the contact of two solutions, a_1 and a , the activities of cadmium-, zinc-, nickel-, and cobalt-salts, and also Λ_C and Λ_A are the ionic conductances of the cation and of the anion, and V_C and V_A are the valences of the cation and of the anion respectively, the term Λ_A was replaced by the mean value of the two anion conductances.

Experimental.

Cyanides of cadmium, zinc, nickel and cobalt were prepared from the dilute solutions of corresponding potassium salt by precipitating with purified sulphates of these metals respectively. Potassium salts used were

(1) This Bulletin, **5** (1930), 345.
(2) *Z. physik. Chem.*, **43** (1903), 735.
(3) Noyes and Sherrill: Chemical Principles, p. 263 (1922).

of Kahlbaum and purified by recrystallization. The precipitated salts were further purified by washing with conductivity water.

Cadmium chloride, zinc chloride, nickel nitrate, and cobalt nitrate were purified by washing five times with conductivity water. Conductivity water used in the experiments had a specific conductance of 1.5×10^{-6}.

The amalgams were made by electrolysing a 10% solutions of pure cadmium sulphate, zinc sulphate, nickel nitrate, and cobalt nitrate with mercury as a cathode, and the amalgams contained about 2.5% of metals. The cells used were of ordinary form. The electromotive force of the cells were measured after being kept in a thrmostat at $18° \pm 0.1$ for about one hour. Constants necessary to carry out the calculation are given in the Tables 1 and 2.

Table 1.

Salt	Moles per litre of water	Activity coeff.	Activity
$CdCl_2$	0.01	0.532(1)	5.32×10^{-3}
$ZnCl_2$	0.0033	0.799(2)	2.63×10^{-3}
$Ni(NO_3)_2$	0.005	0.776(3)	3.88×10^{-3}
$Co(NO_3)_2$	0.01	0.380(4)	3.80×10^{-3}

Table 2.

Ion	Ionic Conductance at 18°C.	Ion	Ionic Conductance at 18°C.
Cd^{++}	46.4	Cl^-	65.5
Zn^{++}	47.0	CN^-	58.6
Ni^{++}	44.0	NO_3^-	61.8
Co^{++}	43.0		

The values in Table 2 were taken from the data of Noyes and Falk[5], except that for the cyanide ion which was determined by the following method.

(1) *J. Am. Chem. Soc.*, **41** (1919), 1787.
(2) Lewis and Randall "Thermodynamics" p. 420 (1923).
(3) and (4) The values were calculated from the data of "Thermodynamics" p. 382 (1923).
(5) *J. Am. Chem., Soc.*, **34** (1912), 459.

The conductivity was measured by the ordinary bridge method, using the cell of uniform diameter. The assembly for the measurements consisted of measuring bridge with a thin wire platinum-iridium, resistance wire, oscillater, and a tunable telephone. The slide wire and the resistance box were calibrated before the conductivity work was begun. The cell constants of the conductivity cell were determined with 1/50 normal solution of potassium chloride. The specific conductance of the sodium cyanide solutions were measured at $18° \pm 0.1°$ C. after being kept in the thermostat for one hour. The results are summarized in the Table 3.

Table 3.

Concentration of NaCN	Cell Constant	Specific Conductance		Equivalent Conductance
		appearent	corrected	
1 Mol	0.228	73188×10^{-6}	73186×10^{-6}	73.186
0.1	0.228	7843×10^{-6}	7841×0^{-6}	78.41
0.01	0.228	829.9×10^{-6}	828.4×10^{-6}	82.84
0.001	0.228	95.76×10^{-6}	94.26×10^{-6}	94.26

We obtained 102 as the value of Λ_∞ at the infinite dilution of sodium cyanide by extrapolation from the data in Table 3, and subsequently 58.6 as the value of ionic conductance of CN^-.

Calculation.

The measured electromotive forces are as follows:

	Cell	E at 18°C.
(1)	Cd (amalgam), Cd $(CN)_2$ (sat) ‖ Cd Cl_2 (0.01 M), Cd (amalgam)	0.02700
(2)	Zn (amalgam), Zn $(CN)_2$ (sat) ‖ Zn Cl_2 (0.0033 M), Zn (amalgam)	0.08705
(3)	Ni (amalgam), Ni $(CN)_2$ (sat) ‖ Ni $(NO_3)_2$ (0.005 M), Ni (amalgam)	0.04300
(4)	Co (amalgam), Co $(CN)_2$ (sat) ‖ Co $(NO_3)_2$ (0.01 M), Co (amalgam)	0.05050

We have the equation (3) by adding the equations (1) and (2).

$$E = E_c - E_l = \left[\frac{1}{2} - \frac{\frac{\Lambda_C}{V_C} - \frac{\Lambda_A}{V_A}}{\Lambda_C + \Lambda_A} \right] \frac{RT}{F} \ln \frac{a_2}{a_1} \quad \cdots\cdots\cdots (3)$$

(1) For the 0.01 molal solution of cadmium chloride, the value of activity a_2 is 5.32×10^{-3} and the values of Λ_C and Λ_A at 18°C. are 46.4 and 62.05, respectively and

$$0.02700=\left[\frac{1}{2}-\frac{\frac{46.4}{2}-62.05}{46.4+62.05}\right]0.0577\ \log\frac{5.32\times10^{-3}}{a_1}$$

then, we obtain

$$a_1=1.51\times10^{-3}$$

(2) For the 0.0033 molal solution of zinc chloride, the value of activity is 2.63×10^{-3} and the value of Λ_C and Λ_A at 18°C. are 47 and 62.05. Therefore,

$$0.08705=\left[\frac{1}{2}-\frac{\frac{47}{2}-62.05}{47+62.05}\right]0.0577\ \log\frac{2.63\times10^{-3}}{a_1}$$

then

$$a_1=4.49\times10^{-5}$$

(3) For the 0.005 molal solution of nickel nitrate, the value of activity is 3.88×10^{-3} and the values of Λ_C and Λ_A at 18°C. are 44 and 60.2. Then,

$$0.0430=\left[\frac{1}{2}-\frac{\frac{44}{2}-60.2}{44+6.02}\right]0.0577\ \log\frac{3.88\times10^{-3}}{a_1}$$

and

$$a_1=5.35\times10^{-4}$$

(4) For the 0.01 molal solution of cobalt nitrate, the value of activity is 3.80×10^{-3} and the values of Λ_C and Λ_A at 18°C. are 43 and 60.2, therefore,

$$0.0505=\left[\frac{1}{2}-\frac{\frac{43}{2}-60.2}{43+60.2}\right]0.0577\ \log\frac{3.80\times10^{-3}}{a_1}$$

and

$$a_1=3.77\times10^{-4}$$

Summary

(1) Ionic conductance of CN^- was determined.

(2) The activities, i.e. solubilities of cyanides of cadmium, zinc, nickel, and cobalt were calculated.

The author expresses his hearty thanks to Prof. J. Sameshima for his kind inspection of this paper.

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OBSERVATIONS ON THE ABSORPTION SPECTRA OF THE RARE EARTHS. I.

By Yasumitsu UZUMASA and Hisateru OKUNO.

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It has been confirmed by several investigators that the absorption bands of neodymium shift toward the longer wave-lengths by increasing the concentration and Beer's law holds only from a definite concentration down. Selwood[1] recently observed that for neodymia and other rare earths investigated increasing concentration is accompanied by a change of molecular volume and molecular refraction and a slight shift of absorption bands. He explained the phenomenon on the basis of the theory of the deformation of the electron shells. It is also well known that the bands of neodymium salts are shifted toward the red on the addition of a common ion. As Quill and Selwood with Hopkins[2] have concluded there may be more than one influence to deal with the phenomenon but the changes of the bands produced here may be possibly attributed to the deformation of the electron shells again since the shifts become more apparent with increasing amount of a common ion added. Changes somewhat similar to those produced on the addition of a common ion are expected to appear if the oppositely charged ions, i.e., Nd^{+++} and NO_3^- for example, are brought close enough to one another to cause distortion of the electron arrangement by any other means than changing concentration or adding a common ion and this will be performed by using a solvent having a smaller dielectric constant than water. Jones[3] studied the absorption spectra of the solu-

(1) *J. Am. Chem. Soc.*, **52** (1930), 3112, 4308.
(2) Ibid., **50** (1928), 2929.
(3) Carnegie Institution of Washington Publication, No. 130, No. 160.

tions of the rare earths and some other comparatively rarer elements and suggested the formation of solvates. No observations were made, however, as to the existence of any general relation between the changes of the bands and the nature of the solvents used. H. Schaeffer[1] states that the absorption spectra of the rare earths are influenced by solvents, both organic and inorganic, and the displacements of the bands caused by the solvents with the lowest refractive indices are in general the greatest. Schaeffer's experiments were carried out with neodymium and didymium. Didymium is as well known a mixture of impure neodymium and praseodymium while neodymium used in his investigation is not believed to be absolutely free from other earths. It was therefore desired in the present investigation to examine conclusively if the changes of the bands are connected with any properties of the solvent used when the observations are made with pure neodymium.

Experimental.

The spectra were photographed by a Hilger spectrograph of constant deviation type and also by a Zeiss hand spectroscope combined with a camera, using a tungsten incandescent lamp as the source of illumination. A Baly absorption tube with quartz end plates was used throughout. The neodymium and praseodymium were purchased from Adam Hilger Ltd. They are the oxides prepared by Luigi R lla and believed by him to have not more than 0.01% total impurities.

Neodymium- and praseodymium nitrates in various organic solvents.

Nitric acid was added to 0.15 gr. pure neodymium oxide until the latter completely dissolved. After the excess of the acid was removed by evaporation the salt was dissolved in water and diluted to 50 c.c. The same amount of the oxide was converted into nitrate in the similar way and the salt dissolved in 50 c.c. pure acetone, thus the concentration of the two solutions being exactly the same, i.e., 0.019 mol. When these two solutions were compared with the spectrograph, there were observed in the acetone solution unmistakable broadenings and shifts of the bands toward the red. As will be seen in Fig. 1, the band at 5800 Å region becomes so markedly intensified in the acetone solution that one may take it more concentrated with respect to neodymium than the water solution. Again a series of nitrate solutions was prepared, using glycerol, methyl alcohol, ethyl alcohol and acetone as

(1) *Physik. Z.*, **7** (1906), 822.

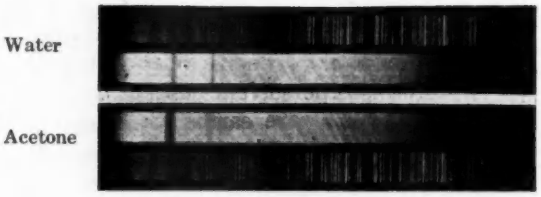

Fig. 1. Absorption bands of neodymium nitrate.

solvent respectively and their spectra were examined. Since each of them contains 0.15 gr. of neodymium as oxide, their concentrations should be the same while their bands are as shown in Fig. 2 more or less shifted and diffused toward the red. All these photographs were taken through 25 mm. of the solutions.

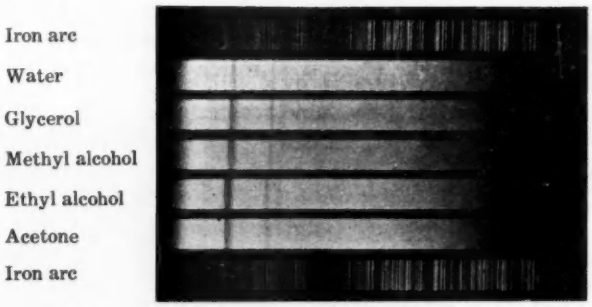

Fig. 2. Absorption bands of neodymium nitrate dissolved in various solvents.

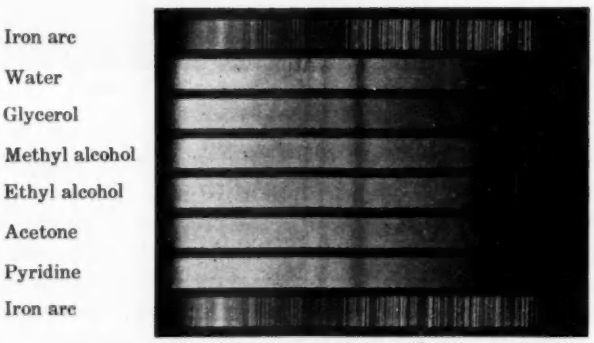

Fig. 3. Absorption bands of praseodymium nitrate dissolved in various solvents.

The similar effect was observed with praseodymium. Fig. 3 shows the absorption bands of praseodymium nitrate in water, glycerol, methyl alcohol, ethyl alcohol, acetone and pyridine respectively. Each solution contains 0.15 gr. of praseodymium as oxide and the spectrograms were taken through 30 mm. of the solution. The displacements are not so distinct as with neodymium but all the bands are more or less broadened and diffused, the effect being most pronounced in the acetone and pyridine solutions. The shift of the narrow band at 4819 Å can be most easily observed.

Influence of common ion in acetone solution.

It was next desired with interest to examine the influence of magnesium nitrate on the bands of neodymium nitrate in the acetone solution. As reported in the paper of Quill and others[1] magnesium nitrate as well as nitric acid produces a marked effect of displacing the bands of neodymium nitrate toward the red. Fig. 4 shows the shifts produced by magnesium nitrate in the water solution, the concentration of which is 0.012 mol. with

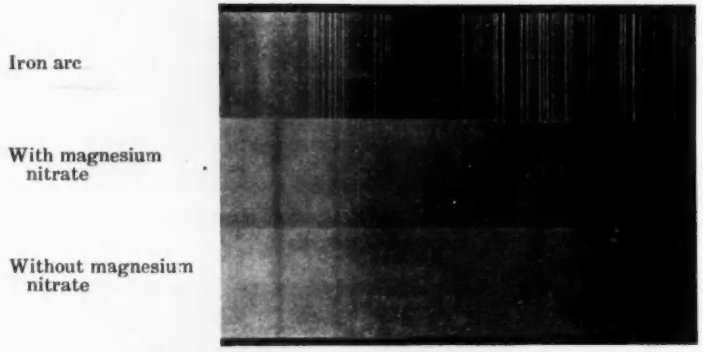

Fig. 4. Absorption bands of neodymium nitrate dissolved in water.

respect to neodymium and 0.496 mol. with respect to magnesium. The photographs were taken through a depth of 70 mm. When acetone is used as solvent, the broadenings take place in the presence of magnesium nitrate in a slightly different manner. The solution contains the same amount of neodymium and magnesium and was photographed through the same depth as before, i.e., 70 mm., while all the bands are more or less broadened and above all the band at 5750 Å region is unmistakably spread out on both sides.

(1) loc. cit.

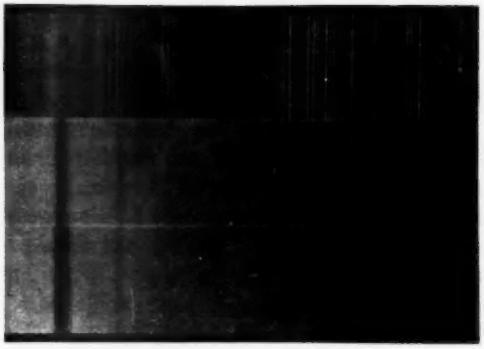

Fig. 5. Absorption bands of neodymium nitrate dissolved in acetone.

Discussion.

It was found in the present investigation that the displacements of neodymium bands are most pronounced when acetone or ethyl alcohol is used while the shifts produced by methyl alcohol or glycerol are less marked, the effect of the latter being the smallest. In the accompanying table are shown the displacement of the bands at 5800 Å in various solvents and the refractive indices of these solvents. No regularity can be observed between these two quantities, however.

Table

Solvent	Shift of the band at 5800 Å region (1)	Refractive index (20°C) (2)	Dielectric constant (20°C) (3)
Water	0	1.333	80.0
Glycerol	17 Å	1.4729	43.0
Methyl alcohol	26 Å	1.329	33.7
Ethyl alcohol	43 Å	1.361	25.7
Acetone	43 Å	1.3591	21.4
Pyridine	—	1.509	12.5

The oppositely charged ions may approach to one another with decreasing dielectric constant of the solvents in which they dissolve. If the defor-

(1) The measurements are approximate as the edges are diffused.
(2) International Critical Tables, Vol. I.
(3) ibid., Vol. VI.

mation of the electron shells should cause the changes of the absorption bands, these changes might be the greatest when the solvent with the largest dielectric constant is used. The present investigation shows that this is exactly the case. As shown in the third column of the table, the dielectric constants decrease as the shifts increase. No photometric examinations were made with the spectrograms taken and it seems rather hasty to postulate any quantitative relation between these two quantities. In view of what has been observed, however, it is suggested that the displacement produced is possibly connected with the dielectric constant of the solvent.

Addition of magnesium nitrate to the acetone solution of neodymium nitrate produces a considerable change, not similar but slightly different from that produced in the water solution. Dissociation of neodymium nitrate as well as magnesium nitrate is supposed to be very small in the acetone solution and the effect of magnesium nitrate thus added may greatly differ from that of the so-called "common ion" added to the dilute water solution. It is still probable that the salt added may affect the electron arrangement of neodymium somehow so that it produces a change in the absorption spectra. It is known that for a given normality the changes produced by magnesium nitrate are slightly more pronounced than those produced by nitric acid. This fact suggests that a metal ion, dissociated or undissociated, might play a part. The further investigation is under way with the intension of finding the influence of foreign substances on the bands of neodymium.

The writer wishes to express his appreciation to Professor G. Nakamura for the use of the spectrograph.

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THE REACTION BETWEEN BENZYL CHLORIDE AND WATER.

By Toshizo TITANI and Katsuzo KURANO.

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The heterogeneous reaction which takes place at a liquid-liquid interface has been studied by several workers. In the majority of these cases, however, at least one of the reactants is solute molecules or ions dissolved in two immiscible solvents.

The object of the following experiments is to investigate the case where the immiscible liquids themselves react with each other at there interface. The reaction chosen as one of such cases was the hydrolysis of benzyl chloride by water according to the equation:

$$C_6H_5 \cdot CH_2Cl + H_2O \rightarrow C_6H_5 \cdot CH_2OH + HCl.$$

This reaction has been already studied by G. Harker,[1] who observed rather remarkable facts that benzyl chloride is not acted on by steam but decomposed by water with constant velocity. The present authors were interested to investigate the course of the reaction with water phase as well as vapour phase, of which only the former reaction is here published as they are obliged to interrupt the experiment. Since benzyl chloride is known to be practically insoluble in water, it will be sufficient to take only the surface reaction in consideration. In the present experiment a known volume of distilled water has been placed on the top of benzyl chloride, the former being stirred with constant rate, and the concentration of hydrochloric acid in it has been determined frequently at different intervals by measuring its electrical conductivity.

Measurements.

A hard glass powder bottle of half liter capacity whose cross-sectional area is 40.0 sq. cm. was used as a reacton vessel. The vessel was closed with a cork stopper holding a thermometer (T), a platinum electrode (E), a small glass stirrer (S) and a fine glass tube (I), as is shown in Fig. 1, b. The two blades of the stirrer stand vertical so as not to disturb the interface of the two liquids.

A weighed quantity of 250 c.c. of distilled water is placed in the reaction vessel which is immersed right up to the neck in a water thermostat. On the other hand a pear shaped vessel (B) with a glass stopper, in which 50 c.c. of benzyl chloride (Schering-Kahlbaum's purest for scientific purposes) is placed, is also immersed in the thermostat. To the bottom opening of the above vessel (B) is connected a rubber tubing (R) with a rubber clip (P) and a glass tube (I), the latter being placed in the reaction vessel through the cork stopper. When the temperature becomes constant the pear shaped vessel (B) is somewhat lifted up and by opening the rubber clip (P) benzyl chloride is allowed to flow into the bottom of the reaction vessel. The tube (I) is then lifted slightly above the interface in order not to disturb it. The stirrer (S) is then started.

(1) *J. Chem. Soc.*, **125** (1924) 500.

The upper end of the stirrer rod is connected through a short rubber tubing (C) co-axial with a pivot of a wooden pulley, which is coupled with another wooden pulley fixed to the axis of a large stirrer of the thermostat. Since the thermostat-stirrer is driven by a small electric motor and regulated so as to rotate with constant rate (100 turns per min.), the rate of rotation of the glass stirrer in the reaction vessel can be controlled at will by choosing a pair of wooden pulleys having a suitable ratio of diameters.

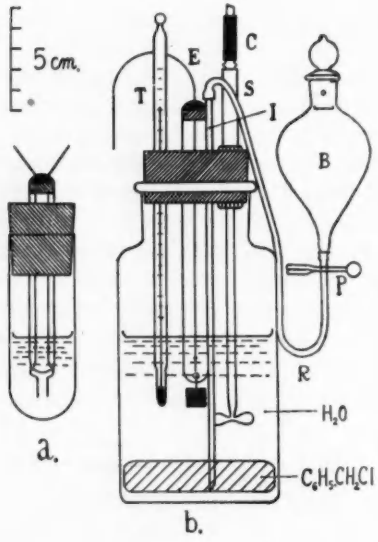

Fig. 1.

The electrical conductivity of the aqueous layer was successively measured by means of a well calibrated Wheatstone's bridge with simultaneous record of time. The concentration of hydrochloric acid was calculated in mol/liter from the observed specific conductance by dividing it with the corresponding molecular conductance and multiplying with 1000. The viscosity of the reacted solutions was found to be identical with the hydrochloric acid solution of the same concentration and distilled water in the limits of the experimental errors.

The necessary data of molecular conductance were determined by the writers at 30° and 50°C. The reaction vessel itself was used as a conductivity cell at 30°C., but as it required a considerable amount of solutions, a

30.0° C.

m	0.000168	0.0002958	0.0005915	0.001183	0.005915	0.001183	0.05915
Λ	450	449	447	450	448	441	423

50.0° C.

m	0.000333	0.000998	0.00333	0.00998	0.0333	0.0998
Λ	570	570	570	560	540	506

small cell with the same electrode (shown in Fig. 1, a) was specially made for this purpose at 50°C. The values obtained are given in the following table, where m expresses the concentration of hydrochloric acid in mol/liter and Λ stands for the molecular conductance.

The conductivity measurement was started when the concentration of hydrochloric acid reached the lower limit of concentration in the control measurement of molecular conductance given above, namely $m = 0.000168$ at 30.0°C. and $m = 0.000333$ at 50.0°C. At first an experiment was done at 18°C. by using the molecular conductance data of Goodwin and Haskell,[1] but the rate of reaction at this temperature was so small that it required whole day to reach the limit just mentioned. All the other experiments, therefore, were carried out at 30° and 50°C., where this period varied from two hours to half an hour according to the temperature and the speed of stirring. Some of the results of the experiments are shown, as examples, by the curves in Figs. 2 and 3, where the figure on each curve indicates the number of revolution of the stirrer per minute. Full data will be given in later tables.

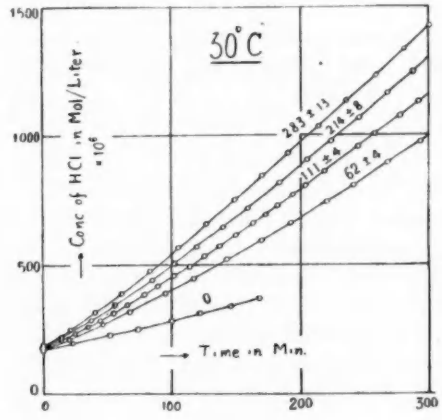

Fig. 2.

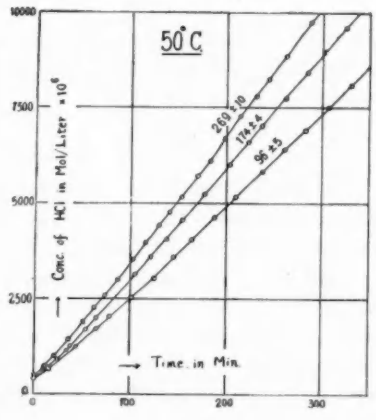

Fig. 3.

It will be seen from these curves that the rate of increase of hydrochloric acid is largely affected by the speed of stirring and, moreover, it increases with time, tending to become constant gradually.

(1) *Phys. Rev.*, **19** (1904), 369.

Results and Discussion.

The experimental results may be accounted for by assuming an adsorption film (A.F.) and a diffusion film (D.F.) in the aqueous part along the interface with benzyl chloride, as is shown in Fig. 4. These films may be movable as a whole but any configurations in the interior of them are supposed to be just like as on solid adsorbents.

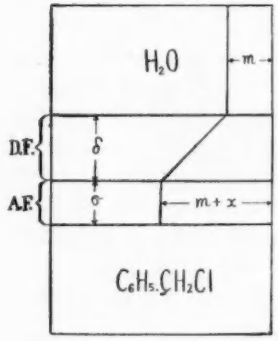

Fig. 4.

Since the reaction is a surface one and adsorbed molecules at the interface are supposed to hinder the progress of hydrolysis, its rate may be expressed by $H-kx$, where x denotes the concentration of adsorbed molecules of hydrochloric acid, H and k being constants at a given temperature. Let m express the concentration of hydrochloric acid in the bulk of aqueous layer whose volume is V, then the rate of increase of the total amount of hydrochloric acid in it is equal to $V\frac{dm}{dt}$, where t denotes the time. The difference of the above two quantities may be equal to the rate of increase of hydrochloric acid in the adsorption film (A.F.), whose thickness is put as σ:

$$S\sigma\frac{d(m+x)}{dt} = H-kx-V\frac{dm}{dt}, \quad \cdots\cdots\cdots\cdots\cdots (1)$$

where S denotes the area of the interface, $(m+x)$ being the actual concentration of hydrochloric acid in the adsorption film.

On the other hand, the rate of increase of hydrochloric acid in the bulk of the aqueous layer is equal to the amount which passes upwards in unit time through the diffusion film (D.F.). This amount is, however, proportional to the area of the interface S, the diffusion coefficient of hydrochloric acid D in water and the concentration gradient in the diffusion film whose thickness is δ:

$$V\frac{dm}{dt} = \frac{D\cdot S}{\delta}\left\{(m+x)-m\right\} = \frac{D\cdot S}{\delta}x\,. \quad \cdots\cdots\cdots\cdots (2)$$

Solving this equation for x and putting the result in equation (1) we have

$$S\sigma\frac{dx}{dt} = H-V\left(1+\frac{k\delta}{D\cdot S}+\frac{S\sigma}{V}\right)\frac{dm}{dt}\,. \quad \cdots\cdots\cdots\cdots (3)$$

Differentiating equation (2) with regards to t and substituting equation (3) in it we have

$$\frac{d^2m}{dt^2}+\frac{D}{\delta\sigma}\left(1+\frac{k\delta}{DS}+\frac{S\sigma}{V}\right)\frac{dm}{dt}=\frac{D}{\delta\sigma V}H. \quad \ldots\ldots\ldots (4)$$

As the solution of this differential equation we obtain

$$\frac{dm}{dt}=A-Ce^{-Bt}, \quad \ldots\ldots\ldots (5)$$

where C is an integration constant and

$$A=\frac{H}{V\left(1+\frac{k\delta}{DS}+\frac{S\sigma}{V}\right)}, \qquad B=\frac{D}{\delta\sigma}\left(1+\frac{k\delta}{DS}+\frac{S\sigma}{V}\right). \quad \ldots (6)$$

But, since $\frac{S\sigma}{V}$ is very small compared with unity, equations (6) may be written in the form:

$$A=\frac{H}{V\left(1+\frac{k\delta}{DS}\right)}, \qquad B=\frac{D}{\delta\sigma}\left(1+\frac{k\delta}{DS}\right). \quad \ldots\ldots\ldots (7)$$

The relation between m and t is obtained by integrating equation (5)

$$m=At+\frac{B}{C}e^{-Bt}+K, \quad \ldots\ldots\ldots (8)$$

where K is an integration constant.

Equation (8) was tested by comparing the calculated values of m with those observed. The results are very satisfactory as is shown in the following tables, in which N denotes the number of revolution of the stirrer per minute. The constants in equation (8) were computed in the following manner: The value of A which is equal to the reaction rate after sufficiently long time (cf. eq. (5)), can be directly known from the slope of the straight portion of the $t-m$ curve shown for example in Figs. 2 and 3. Then by plotting the value of log $(A-dm/dt)$ against the time t we obtain a straight line (cf. eq. (5)), whose slope gives the value of B, C being known from the point of the line on the abscissa.

18.0°C. $N = 109 \pm 2$*

$A = 1.00 \times 10^{-6}$
$K = 978 \times 10^{-6}$

t min.	$m \times 0^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	980.8	978	−3
32	1014	1010	−4
72	1047	1050	+3
98	1071	1076	+5
128	1109	1106	−3
163	1144	1141	−3
203	1179	1181	+2
248	1225	1226	+1

* Continued from the last day.

30.0°C. $N = 0$.

$A = 1.69 \times 10^{-6}$, $B = 0.00352$,
$C = 0.689 \times 10^{-6}$, $K = -22 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	170.7	173	+2
23	199.3	197	−2
52	230.2	229	−1
74	251.3	254	+3
100	285.4	284	−1
122	313.1	311	−2
146	340.3	342	+2
168	370.2	370	0

30.0°C. $N = 62 \pm 2$.

$A = 3.90 \times 10^{-6}$, $B = 0.00440$,
$C = 1.897 \times 10^{-6}$, $K = -260 \times 10^{-6}$,

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	173.4	172	−1
13	199.3	198	−1
22	218.3	218	0
33	242.4	242	0
45	270.6	270	−1
55	293.0	294	+1
66	319.4	320	+1
77	346.7	348	+1
92	385.8	387	+1
110	434.8	435	0
125	476.4	477	+1
143	526.9	528	+1
163	586.0	587	+1
179	633.4	634	+1
194	680.6	681	0
208	723.8	725	+1
227	787.2	785	−2
246	846.3	846	0
267	914.7	914	−1
280	957.9	958	0

30.0°C. $N = 62 \pm 1$.

$A = 3.82 \times 10^{-6}$, $B = 0.00440$,
$C = 1.910 \times 10^{-6}$, $K = -260 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	175.3	175	0
20	213.2	214	+1
47	270.6	273	+2
68	318.6	322	+3
95	391.4	389	−2
117	447.3	447	0
143	521.8	518	−4
170	595.5	596	0
192	661.8	661	−1
220	743.4	745	+2
241	805.7	811	+5
268	893.7	898	+4
294	975.0	982	+7

30.0°C. $N = 60 \pm 2$.*

$A = 3.77 \times 10^{-6}$, $K = 4219 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	4215	4219	+ 4
18	4281	4287	+ 6
42	4383	4377	− 6
66	4473	4468	− 5
85	4528	4539	+11
104	4624	4611	−13
121	4663	4675	+12
140	4764	4747	−17
163	4848	4834	−14
193	4936	4947	+11
215	5050	5029	−21
253	5145	5173	+28
273	5243	5248	+ 5
295	5335	5331	− 4
319	5425	5422	− 3
346	5518	5523	+ 5

* Continued from (62±1) over a night.

30.0°C. $N = 101 \pm 5$.

$A = 4.01 \times 10^{-6}$, $B = 0.00449$, $C = 1.845 \times 10^{-6}$, $K = -224 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	186.4	187	+1
17	224.5	225	0
36	269.2	270	+1
55	314.9	318	+3
73	361.7	366	+4
92	421.5	417	−5
111	476.4	471	−5
137	553.5	548	−6
154	598.8	600	+1
171	656.1	653	−3
188	706.0	707	+1
206	765.2	765	0
224	823.9	824	0
241	876.6	881	+4
262	946.2	953	+7
281	1015	1018	+3
304	1096	1100	+4

30.0°C. $N = 111 \pm 4$.

$A = 4.03 \times 10^{-6}$, $B = 0.00640$, $C = 1.688 \times 10^{-6}$, $K = -89 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	176.7	175	−2
14	210.7	209	−2
25	236.2	237	+1
35	260.9	263	+2
45	288.3	290	+2
55	313.1	317	+4
66	347.5	350	+2
79	387.2	388	+1
89	416.7	419	+2
102	457.6	459	+1
114	493.6	497	+3
126	534.6	537	+2
137	573.1	573	0
150	617.0	616	−1
163	660.1	661	+1
173	693.6	695	+1
182	728.6	726	−3
194	770.5	769	−2
204	805.7	805	−1
219	860.2	859	−1
245	956.1	953	−3
258	1002	1002	0
278	1074	1076	+2
292	1130	1129	−1

30.0°C. $N = 161 \pm 5$.

$A = 4.15 \times 10^{-6}$, $B = 0.00972$, $C = 1.852 \times 10^{-6}$, $K = -26 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	165.0	165	0
20	212.8	211	−2
43	277.4	278	+1
64	340.3	342	+2
83	401.4	403	+2
107	485.7	485	−1
142	608.8	611	+2
163	685.8	689	+3
181	757.9	758	0
202	840.4	839	−1
225	928.5	929	0
247	1015	1016	+1
267	1094	1096	+2
288	1173	1171	−2
310	1274	1269	−5
333	1366	1364	−2

30.0°C. $N = 209 \pm 3$.

$A = 4.36 \times 10^{-6}$, $B = 0.00979$,
$C = 1.709 \times 10^{-6}$, $K = -10 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	166.5	166	−1
11	195.7	196	0
22	228.3	228	0
31	254.9	255	0
45	297.8	299	+1
56	332.0	336	+4
71	388.6	388	−1
84	434.8	434	−1
99	489.2	489	0
110	532.0	530	−2
123	579.2	579	0
134	620.4	622	+2
146	667.4	670	+3
169	764.2	765	+1
180	806.9	806	−1
192	858.8	855	−4
206	913.1	912	−1
220	969.8	970	0
231	1015	1016	+1
246	1081	1080	−1
261	1144	1143	−1

30.0°C. $N = 214 \pm 8$.

$A = 4.31 \times 10^{-6}$, $B = 0.00921$,
$C = 1.796 \times 10^{-6}$, $K = -11 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	184.5	184	−1
14	220.5	220	−1
38	288.3	290	+2
56	346.7	346	−1
85	441.9	442	0
102	505.0	505	0
120	569.0	571	+2
140	644.6	646	+1
159	718.1	719	+1
184	817.7	818	0
205	904.1	903	−1
224	978.4	979	+1
246	1068	1069	+1
268	1163	1161	−2
288	1245	1244	−1
305	1317	1316	−1
325	1405	1400	−5

30.0°C. $N = 283 \pm 13$.

$A = 4.55 \times 10^{-6}$, $B = 0.01117$,
$C = 1.514 \times 10^{-6}$, $K = 48 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	187.3	190	+3
21	250.2	249	−1
41	316.7	313	−4
61	391.4	387	−4
83	476.4	472	−4
105	567.8	568	0
127	660.1	657	−3
149	750.6	750	−1
170	842.9	845	+2
190	930.3	931	+1
214	1034	1034	0
236	1134	1141	+7
259	1231	1228	−3
281	1336	1340	+4
301	1423	1423	0
325	1530	1529	−1

30.0°C. $N = 283 \pm 3$.

$A = 4.50 \times 10^{-6}$, $B = 0.01117$,
$C = 2.084 \times 10^{-6}$, $K = -20 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	166.0	167	+1
11	194.8	195	0
23	230.7	228	−3
35	264.1	264	0
48	304.4	304	0
60	346.7	346	−1
72	391.4	388	−3
84	433.1	431	−2
96	476.4	476	0
108	521.8	522	0
121	573.7	573	−1
135	628.3	628	0
151	690.9	695	+4
166	756.8	756	−1
182	822.6	824	+1
198	890.8	892	+1
213	956.1	956	0
235	1049	1052	+3
253	1131	1129	−2

50.0°C. $N = 96 \pm 5$.

$A = 24.31 \times 10^{-6}$, $B = 0.0237$,
$C = 8.792 \times 10^{-6}$, $K = 52 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	425.1	423	− 2
15	674.2	677	+ 3
44	1251	1253	+ 2
65	1706	1712	+ 6
79	2036	2029	− 7
101	2539	2534	− 5
125	3127	3110	−17
145	3596	3589	− 7
164	4040	4047	+ 7
188	4632	4627	− 5
210	5164	5160	− 4
238	5826	5839	+13
261	6403	6397	− 6
283	6923	6933	+10
307	7508	7515	+ 7
331	8091	8098	+ 7
358	8754	8756	+ 2

50.0°C. $N = 174 \pm 4$.

$A = 29.53 \times 10^{-6}$, $B = 0.0283$,
$C = 11.00 \times 10^{-6}$, $K = 13 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
0	401.4	401	0
14	688.2	687	− 1
24	918.1	919	+ 1
38	1269	1267	− 2
54	1692	1692	0
65	1998	1995	− 3
105	3127	3134	+ 7
121	3596	3600	+ 4
138	4060	4059	− 1
154	4559	4566	+ 7
177	5226	5234	+ 8
203	6012	6009	− 3
223	6587	6600	+13
237	7023	7012	−11
262	7746	7750	+ 4
285	8433	8429	− 4
304	8989	8991	+ 2
325	9614	9611	− 3
348	10310	10293	−17
370	11000	10943	−57

50.0°C. $N = 269 \pm 10$.

$A = 33.64 \times 10^{-6}$, $B = 0.0279$,
$C = 12.42 \times 10^{-6}$, $K = 50 \times 10^{-6}$.

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc)	Δ
0	493.2	496	+ 3
11	744.0	748	+ 4
21	1015	1005	−10
36	1438	1424	−14
51	1893	1874	−19
63	2271	2246	−25
74	2569	2596	+27
87	2998	3016	+18
103	3523	3540	+17
116	3966	3971	+ 5
130	4420	4435	+15
141	4760	4803	+43
153	5164	5204	+40

50.0°C. $N = 269 \pm 10$.

(Continued)

t min.	$m \times 10^6$ (obs.)	$m \times 10^6$ (calc.)	Δ
170	5719	5773	+54
183	6220	6210	−10
198	6699	6714	+15
214	7268	7250	−18
231	7788	7822	+34
244	8258	8260	+ 2
262	8880	8865	−15
288	9743	9739	− 4
316	10730	10680	−50
337	11450	11390	−60
359	12100	12130	+30
383	13010	12940	−70

Table of Constants.

Temp.	N	$A\times10^6$	B	$C\times10^6$	$K\times10^6$
18.0°C.	109± 2*	100	—	—	978
30.0°C.	0	1.69	0.00352	0.689	− 22
	62± 2	3.90	0.00440	1.897	−260
	62± 1	3.82	0.00440	1.910	−260
	60± 2*	3.77	—	—	4219
	101± 5	4.01	0.00449	1.845	−224
	111± 4	4.03	0.00640	1.688	− 89
	161± 5	4.15	0.00972	1.852	− 26
	209± 3	4.36	0.00979	1.709	− 10
	214± 8	4.31	0.00921	1.796	− 11
	283±13	4.55	0.01117	1.514	48
	283± 3	4.50	0.01117	2.084	− 20
50.0°C.	96± 5	24.31	0.0237	8.792	52
	174± 4	29.53	0.0283	11.00	13
	269±10	33.64	0.0279	12.24	50

* After sufficiently long time.

It will be seen from the above tables that the values of A and B increase not only with rise of temperature but also with the speed of stirring. And, moreover, the effect of stirring on A is more prominent at higher temperatures. On the contrary the same effect on B decreases with rise of temperatures, showing a tendency that B becomes independent of the speed of stirring at sufficiently high temperatures. These facts may be accounted for by equation (7) at least qualitatively, taking into considerations the fact that the const nts H and k have a property of reaction coefficient and δ, the thickness of the diffusion film, becomes smaller when the speed of stirring increases.

It is clear from the above data that the reaction is not of zero order as was mentioned by Harker. The reaction can be supposed quite naturally to be of constant velocity if we neglect the adsorption and assume the reaction to be completely irreversible. Nevertheless the result of experiments makes it necessary to assume the presence of an adsorption layer and the hindrance of reaction by adsorbed molecules.

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